INTERNATIONAL ENERGY AGENCY

PROGRAMME OF RESEARCH, DEVELOPMENT AND DEMONSTRATION ON PEAT PRODUCTION AND UTILIZATION

ANNEX 1

Cooperation in Assessment, Planning and Implementation for Research, Development and Demonstration on Peat Production and Utilization.

Stage 1 Report of Subtask II: Fundamentals in Peat Dewatering

(Subtask of Canada)

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ABSTRACT

This report summarizes activities carried out by Canada as a participant with Finland, Ireland and Sweden in a programme of research, development and demonstration on peat production and utilization under the auspices of the International Energy Agency. Under Stage 1 of this Programme Canada assumed the leading role in investigation of the fundamentals of peat dewatering.

The report précis an investigation conducted for the National Research Council of research in other areas where the research methods or results hold potential for transfer to the dewatering of peat. It presents synopses of the lectures presented at an international workshop held in conjunction with a peat symposium at Rivière-du-Loup, Quebec in June, 1985. A significant part of the report deals with the problems of water retention in peat and the reflections, perspectives and recommendations for dealing with these problems through research as viewed by one of the world's leading peat scientists.

RÉSUMÉ

Le présent rapport résume les activités du Canada en tant que participant, avec la Finlande, l'Irlande et la Suède, à un programme de recherche, de développement et de démonstration sur la production et l'utilisation de la tourbe sous les auspices de l'Agence internationale de l'énergie. Dans le premier stade de ce programme, le Canada a dirigé les recherches fondamentales sur l'assèchement de la tourbe.

Le rapport fait état d'une étude effectuée pour le Conseil national de recherches du Canada dans d'autres domaines où les méthodes de recherches ou les résultats présentent des possibilités d'application à l'assèchement de la tourbe. Il renferme des résumés des conférences présentées lors d'un atelier international tenu en même temps qu'un symposium sur la tourbe à Rivière-du-Loup, au Québec, en juin 1985. Une importante partie du rapport porte sur des problèmes de rétention de l'eau dans la tourbe ainsi que sur des réflexions, projections et recommandations d'un des plus grands spécialistes de la tourbe au monde quant à la façon de traiter ces problèmes par la recherche.

INTRODUCTION

In 1983 the International Energy Agency (IEA) agreed to establish a continuing programme of Research, Development and Demonstration on Peat Production and Utilization to promote international cooperation in the field of peat production and utilization.

The participants to the Agreement are Canada, Finland, Ireland and Sweden and tasks undertaken under the Agreement are defined in Annexes to the Agreement. Annex 1 (Task 1) is defined as "Cooperation in Assessment, Planning and Implementation for Research, Development and Demonstration on Peat Production and Utilization". The objective of this task is to obtain, assess and treat pertinent information, to accomplish state-of-the-art studies and to work out plans for future cooperative research, development and demonstration work in the field of peat production and utilization. This objective will be achieved through a number of subtasks:

(a) A review of the state of existing technology in use throughout the world for the production of milled peat and sod peat by solar/wind drying to show potential for improvement;

(b) A state-of-the-art review of fundamentals in peat de-watering, including on-going research, development and demonstration, the assessment of scientific capabilities and formulation of a research distribution strategy;

(c) A study of possibilities to develop new peat de-watering techniques, identifying the national needs for these techniques and systems and on-going work on research, development and demonstration, and including information analyses concerning possible new areas for co-operation among the Participants;

(d) Investigation of the possibility of establishing common classification and standardized methods for peat evaluation;

(e) Evaluation of on-going work on information exchange and preparation of a plan for information exchange among the Participants.

Responsibility for Subtask II, Fundamentals in Peat De-watering, was undertaken by Canada and included planned activities initially as follows:

(i) A state-of-the-art review of global research activities on peat de-watering worldwide, including efforts in fundamental research of related technologies;

(ii) A review of both general and specific scientific capabilities within Participating Countries applicable to the fundamentals of peat de-watering;

(iii) The formulation of a co-operative research strategy to be presented and evaluated at a workshop to be organized by the Canadian Participant after the termination of the review under this Subtask. This strategy would include the distribution of work among the Participants, workshops of both general and specific topics and exchange of research results and of research staff.

Canada, through the National Research Council and extra mural arrangements, completed two significant activities under this task for the purpose of developing a long term strategy for research related to the phenomena of water retention and release in peat. These activities were as follows:

(1) Investigation of transferable technology for application in peat dewatering research.

(2) International Workshop on the relationship of water with peat and its constituents.

This report précis these two significant activities in Part I and II respectively and in Part III offers some direction for future research.

Part 1 of this report is the Executive Summary from the "Final Report on Investigation of Transferable Technology for Application in Peat Dewatering Research" by A. L. Burwash Consulting Ltd., Crozier Information Resources Consulting and D. W. S. Westlake under contract to the National Research Council of Canada. Copies of the full report are available from NRCC on request (NRCC No. 24475).

Part II of this report consists of synopses of the lectures presented at a Workshop on the Relationship of Water with Peat and Its Constituents which formed Part II of Symposium 85, A Technical and Scientific Conference on Peat and Peatlands held in Rivière du Loup, Québec, Canada, 16-20 June, 1985 and sponsored by the Canadian National Committee-International Peat Society and the National Research Council Canada. The synopses are in the order of presentation of the lectures at the Workshop.

Under an agreement with the National Research Council Canada, the complete proceedings of the Workshop will be published as a monograph by Elsevier Applied Science Publishers (EASP), London, England under the title, "Peat and Water: Aspects of Water Retention and Dewatering in Peat". Dr. Charles H. Fuchsman on behalf of NRCC was editor of the manuscript.

Part III of this report presents the Preface and two Chapters of the Workshop publication that deal with matters of particular significance to the IEA task undertaken by Canada concerning peat-water relationships, as follows:

1. The unresolved problems of peat water relationships.
2. The peat-water problem: reflections; perspectives; recommendations.

The contents of Part III represent excerpts provided by Charles H. Fuchsman, Editor, "Peat and Water: Aspects of Water Retention and Dewatering in Peat", under contract with the National Research Council of Canada.

Due to the long-term and basic nature of the research of this subtask Canada has not attempted to rationalize the resources required to implement the recommendations ensuing from this work. With Canada's withdrawal from the Programme, effective March, 1986, the report is presented to continuing IEA programme participants in the hope that it will prove a helpful contribution to the problem of peat dewatering.

PART 1 - FINAL REPORT ON INVESTIGATION OF TRANSFERABLE TECHNOLOGY FOR APPLICATION IN PEAT DEWATERING RESEARCH: EXECUTIVE SUMMARY

FINAL REPORT ON INVESTIGATION OF TRANSFERABLE TECHNOLOGY FOR APPLICATION IN PEAT DEWATERING RESEARCH: EXECUTIVE SUMMARY*

A. L. Burwash Consulting Ltd., Crozier Information Resources Consulting, and D. W. S. Westlake, Calgary, Canada

The project described in this report was initiated in response to a concern recognized and expressed by the International Energy Agency, in which Canada is a member. Fuel-quality peat is found in abundance throughout the world's temperate zone; its use as a fuel is limited by its high moisture content of up to or greater than 90 percent (wet basis). Artificial dewatering technologies presently used on a commercial scale are able to economically remove peat water only to the 75 percent (w.b.) level; further dewatering uses more energy than it releases. Peat dewatering studies, while becoming more sophisticated, have not yet produced sufficient data to provide researchers with a clear understanding of the components or character of peats. Neither are the fundamental mechanisms of dewatering fully understood.

This study was designed to survey and document research that is being done, or that has been completed, in areas where the research methods or results hold potential for transfer to the dewatering of peat. Over 400 research personnel were contacted; government, industry, and university sections were fully represented. Extensive

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* The complete report NRCC No. 24475 is available from Publication Sales and Distribution, National Research Council of Canada, Ottawa, ON, Canada K1A 0R6.

literature searches and reviews were carried out; discussions were held with professionals by telephone and in person. Analysis of the acquired data indicated those areas most relevant to the study; primary researchers readily became apparent.

The report reflects the methodology used by the researchers to attain the project objectives, which were:

- identification of disciplines and subdisciplines in which research work may be transferable to future studies in the fundamental aspects of peat dewatering;
- identification of transferable research results and research methods from each relevant discipline or sub-discipline;
- identification of researchers in universities, government agencies, and companies who have done or are currently doing relevant or transferable research; and,
- provision of a brief explanation of the transferable research as it relates to gaps in knowledge concerning the fundamental aspects of peat dewatering.

The contractors, in identifying research carried out in other fields, and gaps in current knowledge directly related to peat technology, classified the thrust of the project search requirements in the broad areas of:

- State-of-the-Art: Fundamental Aspects of Peat Dewatering
- Microbiology of Peat

- Porous Media Studies
- Physical Chemistry: Principles Actions and Characterization
- Cellulose - Lignin Degradation
- Research on Water-Binding Mechanisms
- Drying Measurements and Modelling

The search for transferable technologies led to examination of work in very diverse fields. The need to examine methods of pore characterization led to primary inquiries in civil engineering, petroleum engineering, physics and chemical engineering. Chemical characterization needs were met in the pulp and paper, textile, and food industries; and in basic chemical research. Movement of fluids in porous media is being researched in civil engineering, chemical engineering, petroleum engineering, and agricultural engineering. The nature of water-holding mechanisms is being studied in fields where high moisture content materials are handled such as agricultural engineering (livestock wastes), mineral engineering (cakes and slurries), chemical engineering (sanitary wastes), and the food industry (drying and preservation of food). Microbial studies are being carried out in biology and chemical engineering departments and forestry research centres.

The search for relevant transferable technologies revealed that:

- Biological and microbially produced compounds could play a significant role in evolving more effective peat dewatering procedures. Changes in the chemical structure of peat may change water-holding capacity.

- Surface chemistry studies have direct application to fundamental research on the way in which water is held in peat.
- Well-established methods for characterization and quantification of pore space are available for use in peat studies with minimal adaptation. The conceptual framework for development and testing of models of pore configuration an fluid flow has been established. Use of these models will require adaptation and further empirical studies to provide the basis for verification.
- Characteriztion of the peat, followed by application of principles used by scientists for other media, will help produce the data required for a comprehensive peat dewatering research program.
- Studies on degradation of peat constituents, chiefly lignin and cellulose, may have indirect benefit in developing innovative dewatering methods.
- Interest in identifying water-holding mechanisms and assessing their relative importance is evident in several disciplines. Basic studies have revealed promising techniques for detection and analysis. Many of these studies, however, are still in preliminary stages.
- Theoretical and experimental work is being conducted on drying of hygroscopic materials. Modelling and measuring techniques are available that could appropriately be transferred to peat research.

The research subjects, methods, and results examined during the project are fully documented in the report. The study has been strongly inter-disciplinary; as a result, it has brought together information from all relevant scientific and technological areas. The depth and array of information available for the use of peat researchers is clearly identified. The task of priorizing and selecting specific research subjects now belongs to the respective bodies under whose auspices this study was conducted.

PART II - WORKSHOP ON THE RELATIONSHIP OF WATER WITH PEAT AND ITS CONSTITUENTS: SYNOPSES

WORKSHOP ON THE RELATIONSHIP OF WATER WITH PEAT AND ITS CONSTITUENTS: SYNOPSES

PLANTS TO PEAT - THE PROCESS OF HUMIFICATION

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The conversion of vegetable matter to peat is a process whose continuation leads to the formation of lignite and various coals. Peat formation is termed humification. Later steps in the sequence include diagenesis, which involves dewatering and compaction. Coal is formed by subsequent metamorphic changes. Throughout coalification the concentration of hydrogen and oxygen was continually decreased, and the carbon content increased. Peat was first used for fuel. In the 19th century it found increasing application in horticulture and agriculture, and now it is also of value in chemical industry and medicine.

The variations in peat arise from the variety of plants whose residues contribute to peat formation, and from the environmental conditions in which humification takes place. Alteration in the mineral content, increasing pressure of overburden, physical transport, goethermal changes, and microbial activities are among the variables which affect the course of humification and produce the diversity observed in peats.

Peat comprises relatively unstable substances. The reactivity of these substances contributes to its usefulness.

Peat is characterized by colloidal behavior, and by irreversible loss of wettability, produced by drying.

The physiological activity of peats is observed in peat-bath therapy of humans and in promotion of growth in some plants.

Non-fuel uses of peat should be given precedence over fuel uses to postpone exhaustion of peat resources.

SOME BASIC PRINCIPLES OF WATER MANAGEMENT IN PEAT

W. Flaig, Gerbrunn, Federal Republic of Germany

Mosses and graminaceous plants are the most important contributors to peat formation. Although the main chemical components of plants are not highly hydrophilic, humification produces physical and chemical changes which make the resulting peat highly water-retentive. The development of a spongelike structure accounts for part of the ability of peat to hold water, while chemical alteration, especially of the lignins, makes the surfaces hydrophilic.

The process of humification is largely mediated by microorganisms which use the carbohydrates from dead plants as food to provide the energy for their growth and metabolism. The process occurs under increasingly anaerobic conditions.

Lignins degrade by oxidation, demethylation, and other reactions producing a sequence of compounds which can, by oxidative coupling, by polymerization, and by condensation with protein residues yield a variety of humic substances. The lignins and their humic reaction products thereby become increasingly resistant to microbial degradation. The rate of lignin degradation can be measured by the evolution of ^{13}C and ^{14}C labeled CO_2.

Because of the complexity of humic substances, experiments on the synthesis of lignin-like polymers from simple dihydric phenols have been useful in elucidating molecular structure.

The chemical composition and physical structure of humic substances are responsible for the water-retention character of peat. These substances are colloidal, usually found as spheroidal aggregates, with fine internal pore structures. Nitrogen in humic substances tends to be associated with decreased pore size, but also with increased degree of hydration.

COMPRESSION AND GRAVITY DRAINAGE AS MEANS OF DEWATERING PEAT

Tuncer B. Edil, Peter B. Bosscher and Calvin B. DeWitt, University of Wisconsin-Madison, Madison, WI, USA.

The dewatering of peat by compression and by gravity drainage, respectively, has been described in relation to the complex structure of the peat. Samples of hemic and fibric peats were used in the studies of deformation as a function of time under compressive stress. Water is initially retained in coarse channels (macropores) and fine pores (micropores). The work required to remove water from the macropores is less than that required to remove it from the micropores.

The variation of compressive strain with time appears to be divisible into four components: an instantaneous strain; a primary strain which develops over about one minute; a secondary strain which occurs over the next 1,000 minutes; and tertiary strain which appears over the next 10,000 minutes. Water outflow from the compressed mass continues after the dissipation of measurable pore water pressure, indicating that water outflow is not wholly controlled by macro-hydrodynamic factors. The time required for the dissipation of this pore pressure increases with each increment of compressive stress, suggesting that at higher stresses both compressibility and permeability decrease.

The decrease in permeability is anisotropic. Permeability in the direction of compression was only 1/300 of the permeability in the plane perpendicular to compressive force.

In tests on constant strain rate, compressive stress was measured at equilibrium conditions, when dewatering occurs at a constant rate. In a fibric peat containing about seventy percent water, a strain rate of 0.2-0.3%/min required a stress at equilibrium of 84-104 kPa. At higher stress rates, equilibrium stress went up appreciably. The typical strain at equilibrium was about 40%.

The concepts of stress-strain equilibrium combined with that of consolidation as measured by dissipation of pore pressure were used to model field drainage of a peat mound based on ditching, with gravity supplying the main compressive stress. By including perturbation by three subsurface springs the model agreed closely with field observations on surface groundwater elevations.

SATURATED AND UNSATURATED PERMEABILITIES OF NORTH GERMAN PEATS*

Michael Loxham, Delft Soil Mechanics Laboratory, Delft, The Netherlands; and Wolfgang Burghardt, Technical University of Essen, Essen, Federal Republic of Germany.

Peat samples from nine different north German peatland sites were used to develop a theoretical representation of the permeability of peat to water flow under saturated and unsaturated conditions. The theories applicable to water movement in mineral soils are not applicable to peats; and the mechanisms of flow in saturated peats differ from those in unsaturated peats.

Microscopically peats reveal a high degree of structural organization, characterized mainly by large channels (macropores) and fine channels (micropores), some of which are discontinuous. At any given level of saturation water movement is greatest in the largest channels available. Thus on drainage, water is lost most rapidly through a few interconnected large channels, and hydraulic conductivity, increasingly restricted to micropores, diminishes.

The effective length of the channels is increased by their tortuous interconnections, the tortuosity being determined in practice, for any given sample, by experimental measurements.

In the mathematical model developed for unsaturated peats, flow through macropores is considered negligible. It is experimentally demonstrable that shrinkage which accompanies the early stages in drainage is attributable to collapse of the large channels without significant change in the fine (micropore) capillaries.

The range in capillary size is very large. For changes of less than 50% in moisture content of the peat, change in permeability may range over five orders of magnitude. Using a shape factor describing

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*This paper was not presented orally at the meeting but is included in the Workshop Proceedings.

the deviation of the cross-section of the channels from circularity, a general equation for permeability is developed. Agreement with experimental observation is quite good for some profiles. In others, however, the derived formula overestimates hydraulic conductivity, probably because there is less interconnection among the pores than the model assumes.

APPLICATION OF A MEMBRANE MODEL TO THE STRUCTURE OF HUMIC MATERIALS IN PEAT

R. L. Wershaw, K. A. Thorn, and D. J. Pinckney, U. S. Geological Survey; P. MacCarthy and J. Rice, Colorado School of Mines; and H. F. Hemond, Massachusetts Institute of Technology, USA

The proposed structure of humic substances is analogous to that of biological membranes rather than consisting of high-molecular weight covalently bonded cross-linked molecules. The analogy presupposes the existence of micellar aggregates with hydrophilic exterior surfaces, and a predominantly hydrophobic interior. The molecules comprising these aggregates are of moderate molecular weights and are bonded by weak forces, e.g., hydrogen bonding, pi bonding, and hydrophobic interactions. The aggregates may exist as small particles, or as more extended sheets coating other mineral surfaces. This structural model includes not only humic acids, but also fulvic acids and humins.

Evidence for this model of weakly bonded aggregation consists largely in the relatively mild requirements to disaggregate these colloidal units by derivatization, by the use of alkali, or various organic solvents. The model is used to explain the sorption and retention of non-polar substances (e.g., DDT) which can be held in the hydrophobic interior of the aggregate, and the extraction of lipids from humins.

The use of a methyl isobutyl ketone extraction step in the humic and fulvic acid extraction procedure results in somewhat greater yields of the acids. The humic acid derived by this solvent modification of the extraction procedure also tends to be more aliphatic than conventionally extracted humic acid.

The model of humic acids as micellar aggregates is used to explain some of the variation in humic acid yields and compositions which result from variations in extraction procedure noted in the published literature.

METAL ION EXCHANGE ON PEAT

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The adsorption and desorption of metal cations in peat is described in terms of equilibrium transfer processes between the cations in the bulk solution exterior to the peat particles and the intraparticle liquid phase. Under the conditions studied, the processes are controlled either by diffusion rate through the surface film or by diffusion through the interstices of the particles.

New experimental data are given for a well-humified sedge peat, rich in humic acids. The humic acids are considered to be the primary metal complexing components in peat. The main adsorption sites are those with neighboring carboxyl and phenolic hydroxyl groups.

Measurements of equilibrium constants and kinetic properties of solutions of cupric ions confirm the model. In practice the desorption of the metal does not appear to be a simple reversal of adsorption, partly because of slow diffusion rates within the interstitial channels of the particles. Adsorption and desorption processes therefore display hysteresis.

Selectivity of peat for some metal cations is illustrated by the displacement of calcium ions by copper ions; and by the failure of sodium ions to displace bivalent cations from peat.

Rate computations of diffusion-limited ion exchange take into account the coupling of chemical potential (generated by a concentration gradient) and the electrical potential (generated by the movement of ions through environments which contain other ions and charged surfaces). The model so developed for intraparticle diffusion is compared with a model for film diffusion-limited movement of ions. Experimental data confirms the validity of the intraparticle model, which thus differs from the conclusions of Bunzl (1974). Bunzl, working with lead adsorption on peat had preferred the film diffusion-limited model.

COLLOID SCIENCE IN PEAT DEWATERING: PRINCIPLES AND APPLICATIONS

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Colloid chemistry is concerned with dispersed systems in which the size range of the dispersed phase is roughly 1-1000 nm. The thermodynamics and rheological properties of such dispersions are affected more by the properties of the relatively large interfacial area than by those of the bulk phase. The dispersed particles characteristically do not settle in any reasonable time. Since interfacial phenomena dominate the properties of colloidal systems, the study of surface properties, even of larger particles, is generally included in the purview of colloid science. This is particularly true in cases in which adsorption affects interparticulate interaction, flocculation, and dewatering.

A brief discussion is presented on the phenomena of electrical double layers, surface and interfacial tension, ion exchange, osmotic pressure, and other factors pertinent to the dewatering of peat.

Experimental work illustrative of these concepts is reported. In dewatering studies on a highly decomposed Nova Scotia high-moor peat, samples (5 cm diameter) were compressed hydraulically at 20 atm for 2.5 minutes to a final thickness of 3.2 mm. Final water concentration was determined by drying. The dewatering of untreated peat was compared with that of peat treated with dodecyl sulfate (an anionic surfactant), with dodecyltrimethylammonium bromide (a cationic surfactant), and with Percol 402, a commercial cationic polyacrylamide. The anionic surfactant had no effect on either water removal or the clarity of the expressed water. The cationic surfactant improved dewatering up to a maximum of 60% (at 8% surfactant based on the dry weight of peat). The water removed from the press under these conditions was clear. At higher concentrations the dewatering was less effective, and the effluent was no longer clear, indicating stabilization of the colloid. The cationic polyacrylamide behaved similarly to the quaternary ammonium salt. These observations correlated well with the measurement of zeta potential in the presence of the respective surfactants.

WATER RETENTION BY HUMIC SUBSTANCES

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A principal feature of humic materials is their ability to absorb and retain large quantities of water. The mechanisms of the reactions of water with humic and fulvic acids have been investigated in terms of water vapor adsorption, surface tension measurements, surface pressure measurements, and electron microscopy.

Water sorption isotherms were similar for both humic acid and fulvic acid at relative humidities (RH) below 60%. At higher RH fulvic acids adsorbed considerably more water than did humic acids. Water adsorption equivalent to monomolecular layer coverage occurred at 33% RH. The increase in water adsorption with higher RH suggests that water molecules are more tightly hydrogen-bonded to each other than to humic and fulvic acids.

Humic and fulvic acids both lower the surface tension of water. The surface tension varies inversely with the concentration of these dissolved substances and with the pH. In general fulvic acid has a more pronounced effect than humic acid on surface tension.

From data on surface pressure the number-average molecular weight for humic acids was calculated to be 1810, while that of fulvic acids was 1040. The respective surface areas of the two acids were 30.0 and 24 m^2/g.

Electron micrographs of humic and fulvic acids showed them to be elongate multibranched fibers 20-100 nm wide with calculated surface areas (at 50 nm fiber diameter) of 53.2 m/g.

Surface area measurements by BET procedures (using N_2 and He) gave low values (2.5 m^2/g) which were attributed to the likelihood that only external surfaces of the humic and fulvic acid particles are measured by the BET method, whereas most water adsorption occurs on internal surfaces.

The surface tension measurements are considered to be most valid for surface area study of humic and fulvic acids.

VARIATION OF HUMIC SUBSTANCES WITHIN PEAT PROFILES

Hamish Anderson and Alan Hepburn, Macaulay Institute for Soil Research, Craigiebuckler, Aberdeen, Scotland

Humic substances were studied in two peat profiles, one an unstratified sedge fen peat; the other well-stratified hill peat derived from woody species and grasses. The problems inherent in operational definitions of humic and fulvic acids based on their solubility in aqueous alkali are noted. The problems are more complex in peats which contain significant amounts of relatively undecomposed plant material than in the B-horizon of podzols whose organic matter is highly humified.

Several products of hydrolysis of peat humic substances are studied for their relevance to molecular structure and to changes occurring during humification. Primary polysaccharides, representing undecomposed plant carbohydrates, can be converted to levulinic acid on prolonged hydrolysis. However, humic substances yield higher levels of levulinic acid then is obtainable by conventional methods of carbohydrate hydrolysis. This excess is attributed to altered carbohydrates, presumably attached to the humic acid molecular structure. Such polysaccharides are identified as secondary. The primary polysaccharides in pyrolysis studies are associated with dianhydromonosaccharide fragments, whereas secondary polysaccharides yield furan fragments.

The process of humification also affects lignin-derived moieties. Conversion of the ether-soluble fractions of peat acid-hydrolysates to volatile trimethylsilyl derivatives permitted separation and quantification of characteristic phenolic acids. 4-hydoxybenzoic acid predominates in undecomposed monocotyledonous plants and mosses; vanillic acid predominates in undecomposed conifers; and a more nearly equal mixture of the two is typical of deciduous dicotyledonous vegetation. A third acid, 3,4-dihydroxybenzoic acid, results from degradation of monocotyledonous lignin by hydroxylation, and from conifer lignin by demethylation. It may thus be possible, by using

appropriate ratios of these acids, to describe the extent of humification and the vegetable origin of the peat.

The fen peat showed a steady increase of non-polypeptide nitrogen with increasing depth.

The loss of some of the phenolic compounds and fulvic acid components by natural drainage of the bog waters may account for the apparent changes in organic content with humification.

CHARACTERISATION OF A BOG PEAT PROFILE BY CURIE POINT PYROLYSIS-MASS SPECTROMETRY, AND BY HIGH RESOLUTION GAS CHROMATOGRAPHY-MASS SPECTROMETRY

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A peat profile of ombrotrophic origin was studied by Curie-point pyrolysis-gas chromatography-mass spectrometry (Pygcms) for structural identification, and by automated pyrolysis mass spectrometry (Pyms) to "fingerprint" the samples. The results were correlated with a paleofloristic analysis, using the light microscope.

Pygcms studies on carbohydrates and lignins provided information on mass peaks from typical undecomposed plant carbohydrates and lignins. These peaks in the mass spectrograms have been identified as known compounds and are useful as markers for peat samples.

A comparison of mass spectra with reference "zero point" spectra yields discriminant scores, which can subsequently be interpreted as the relative abundance or absence of substances characteristic of particular types of degradation and degrees of humification.

Using such techniques it was possible to show that the deposit which was originally formed by ericaceous plants increased in humification from the bottom of the deposit to a point half-way to the surface. This increase in humification is marked by increases in lignin-related residues and decreases in carbohydrate fragments. An abrupt change in climate and environment resulting in less humified sphagnaceous residues characterizing the upper parts of the deposit, are shown by increased carbohydrate residues, and diminished evidence of lignins.

The instrumentation and computerized analyses are described in the paper.

ORGANIC GEOCHEMICAL STUDIES OF THE HUMIFICATION PROCESS IN LOWMOOR PEAT

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Sawgrass peat (formed from Mariscus jamaicensis) found in the Everglades of Florida was investigated by elemental analysis and ^{13}C NMR spectroscopy. The course of humification appears to be characterized by a loss of cellulose and other carbohydrates present in living plants, and an accumulation of humic substances whose aromatic character is traceable to lignin origins.

Conventional separations to yield humic acid, fulvic acid, and humin fractions were considered in the light of cellulose determination made via a holocellulose procedure. The holocellulose and humin fractions appear to be overlapping categories. Evidence of soluble carbohydrate fragments in an acid hydrolysate of humin supports this view.

The peat samples are characterized by a low degree of humification. Consequently much of the humin fraction may be relatively unchanged substances originally present in the living plants.

The substantial quantity of paraffinic material found in both the humin and holocellulose fractions is believed to be of algal or other microbial origin.

In some cases there appears to be a decrease in humic acid content despite an apparent increase in humification, as indicated by the humin content. This decrease of humic acid may be attributable to loss of humic acid fragments by selective oxidation and solution and removal during the course of natural bog drainage.

CUPRIC OXIDE OXIDATION PRODUCTS OF HUMIC ACIDS FROM FINNISH MILLED PEAT

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The oxidative degradation of peat humic acids by cupric oxide in an alkaline medium provides a means for generating identifiable molecular fragments, some of which can be traced to lignin-like components. Such procedures used on lignins generate a characteristic group of 2-methoxy- and 2,6-dimethoxy-phenolic compounds. The presence of these products in CuO-oxidized humic acids provides qualitative evidence of the lignin contribution to humic acid formation. Quantitative estimates of that contribution are also offered, based on a comparison of the yields of phenolic compounds by lignins and humic acids treated under comparable conditions. Previous work on sphagnum peats did not generate lignin-like compounds presumably because sphagnum does not possess lignins of the type found in conifers, deciduous trees, or grasses.

The humic acids were obtained from a Finnish peat which had been dried, ground, sieved, extracted with 0.1N NaOH, and acidified (pH2). The precipitated humic acids were redissolved in NaOH and purified by dialysis. Following oxidation with CuO in the presence of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ in 2N NaOH at 170°C for three hours, the products were fractionated on the basis of solubility in acid, base, ethyl acetate, and water. The fraction studied for lignin fragments was alkali-soluble, acid-soluble, extractable by ethyl acetate, but not extractable with water from ethyl acetate solution. This fraction, equal in weight to 26.6% of the humic acids oxidized, was silylated and subjected to gc and gcms analyses. It is concluded that about 4% of undecomposed birch or spruce lignin is present in the peat humic acid sample studied. The other large fraction of oxidized humic acids (base-soluble and acid-insoluble) is also highly aromatic, judging from proton magnetic resonance data.

THE ROLE OF CARBOHYDRATES IN SOME SOIL ENZYMES

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Carbohydrates represent about 10% of soil organic matter. About 1-2% of the carbohydrates are present in the form of lipoprotein-liposaccharide (LP-LS) complexes, among which are "glycoenzymes". Glycoenzymes are proteins, with covalently bonded carbohydrates, possessing enzymic properties. Although soil enzymes are usually rapidly degraded by other soil proteolytic enzymes, or are inactivated by reaction with humic substances or clay particles, these glycoenzymes can be recovered in active form. Their structure and probable mechanism of formation is therefore of potential significance in soil organic chemistry.

Glycoenzymes with carbohydrase activity are extracted with 0.1M ethylenediaminetetraacetic acid (EDTA) at pH 8.0, and purified of humic colloids by $(NH_4)_2SO_4$ precipitation, dialysis, and salmine or protamine fractionation. The yield of free enzyme (EFS), recovered after lyophilisation, was 50 mg/kg of soil. Alternative extraction by pyrophosphate (at pH 7.0), instead of EDTA, was less efficient.

A fraction, (m.w. 75,000-100,000) comprising 50% of the EFS dry weight, had high invertase activity, as well as significant cellulase, β-D-glucosidase, acid protease, and phosphatase activities.

Analysis of the amino acid residues of EFS show high glycine, alanine, asparagine, threonine, and lysine contents. The carbohydrate portion is characterized by large amounts of glucosamine and galactosamine, along with neutral sugars (especially rhamnose and xylose).

These and other observations lead to a postulated structure for EFS of a polypeptide containing three types of carbohydrate linkage: (1) glycopeptide linkage of N-acetylglucosamine to the amino group of asparagine; (2) glycosylate linkage of N-acetylgalactosamine to the hydroxyl group of threonine; and (3) glycosylate linkage of neutral sugars to the hydroxyl group of serine.

In nature, the third linkage is most reactive, and the neutral sugars are largely lost. The reactive amino acid sites thus uncovered combine with readily available LP-PS produced by Gram-negative soil bacteria, such as Pseudomonas. The resulting reaction envelops the EPS core with a stable LP-PS coating. Lysine residues in the LP-PS react with clays or humic colloids without adversely affecting the active enzymatic sites of the EFS (e.g., the tyrosine, residue essential for invertase activity).

These biochemical reactions may be significant in rationalizing chemical changes occurring in the hydrophilic components of peat soils.

STRUCTURE AND PHYSICAL PROPERTIES OF PEPTIDOPOLYSACCHARIDES RELEASED BY SOIL-INHABITING PENICILLIUM SPINULOSUM AND OTHER SPECIES OF PENICILLIUM

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Penicillium species occur widely in peat, and grow well in the pH range of 2 to 6. Where the pH is below 4, some Penicillium species depend initially on the availability of ammonium ions. On depletion of ammonium, the fungus releases active acid proteases (proteolytic enzymes) and extracellular glycopeptides (peptido-phosphogalactomannan, pPGM). The latter may be formed by the action of the enzyme of glycoproteins. The pPGM is likely to be very active in soil aggregate formation, since it has a chemical structure favorable for binding with soil particles.

The molecular structure of pPGM has been characterized using carbon-13 NMR, phosphorus-31 NMR, circular dichroism spectropolarimetry and various wet chemical procedures.

The pPGM is a polymer of molecular weight approximating 70,000. It consists of a backbone of mannan (a linear polymeric sequence of mannose sugars) to which are attached side chains of galactan (galactose sequences), phosphorylethanolamine units, and polypeptide chains.

Although mannose occurs in higher plants (especially gymnosperms) as well as in microflora; the linkage of successive mannose units to one another is quite different in the two botanical groups. In the higher plants the linkage is beta-1,3 and beta-1,4; whereas in soil fungi it is principally alpha-1,2 and alpha-1,6. It is thus possible to establish the fungal origin of these substances.

The polypeptide chains appear to contain about 30 amino acid residues, with serine and threonine units forming points of attachment, by O-glycosidic linkage, to the sugars. The phosphoryl groups serve as connecting links between the C-6 of mannose units and the N-substituted aminoethanol residues.

PART III - PEAT AND WATER: PREFACE, PROBLEMS, REFLECTIONS, PERSPECTIVES AND RECOMMENDATIONS

(As viewed by Charles H. Fuchsman, 3006 Cedar Lane N.W., Bemidji, Minnesota, USA)

PEAT AND WATER: PREFACE

The chapters of this book* are, with some modification and elaboration, papers presented at Rivière-du-Loup, Québec, on June 19, 1985 . The text has been supplemented by an introduction and summary, offering an overall rationale for the work, pointing out the common themes, and identifying appropriate directions for future work. The original papers, collectively titled "The Relationship of Water with Peat and its Constituents" comprised Part II (Workshop) of Symposium '85, sponsored by the Canadian National Committee of the International Peat Society, and the National Research Council of Canada (NRCC). The symposium was generally supported by many private companies and associations with commercial interests in peat. Part I of Symposium '85, which took place on June 17-18, dealt with a wide range of commercial, engineering, marketing, ecological, and political aspects of peat production. Since the Part I papers are to be published in a separate Proceedings volume**, they are not included here. However the opportunity to listen to and discuss these earlier papers afforded the authors of the present volume additional insights into the practical problems which motivated the more theoretical discussions of June 19.

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*Peat and Water: Aspects of Water Retention and Dewatering in Peat, EASP, London (in press).

**Proc. Symp. '85: Part 1. Resources and Development of Peat and Peatlands, Rivière-du-Loup, Québec, 1985. (T. E. Tibbetts, ed.). (in press). ISBN.

The meeting terminated in a workshop in which fundamental aspects of peat-water relationships were critically reviewed by the authors represented here and by other delegates. Those discussions and the publication of the technical papers comprise part of the NRCC contribution to the International Energy Agency's peat program.

Although problems in peat fuel technology provided the main rationale for this conference, no attempt was made to limit the discussions to energy implications. It was freely conceded, at the outset, that those properties of peat which are pertinent to fuel use are important in non-fuel applications too, and that progress in the understanding of peat-water relationships would be accelerated by expanding the scope of experimental studies in the physics, chemistry, and biology of peat.

The authors*** of the individual chapters represent a wide variety of specialized research experience in academic, government, and private institutions in Europe and North America. Their discussions were further enriched by the participation of delegates from other parts of the world.

Each speaker attempted to communicate, in an intellectually stimulating manner, complex technical concepts and viewpoints to an audience with diverse scientific interests and backgrounds. The final discussion of the workshop confirmed the success of this

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*** Reprint requests and inquiries should be addressed to the authors. For chapters written by more than one person, correspondence should be sent to the first-named author.

interdisciplinary effort. Subsequent modifications of the workshop papers to book chapters were intended to incorporate the understandings gained from the discussions, and to make available to a wide readership the scientific contributions and technical judgements of the authors.

Establishing communication among representatives of different specialities does not, of course, imply that the problems discussed are thereby resolved; but it does mean that the workshop participants and, therefore, the readers of this publication can draw on the resources of many disciplines in their efforts to understand peat, and to use it wisely.

No apologies need to be made for differences in style and format among the individual chapters of this book. The texts have, however, been revised to improve readability, and minor technical errors have been corrected in the course of editing. The abstracts which precede the individual chapters are derived in part from those submitted by the authors. In most cases, however, the abstract has been revised and enlarged by the editor to provide the reader with a more substantial overview of the technical content of the chapter that follows.

The order of the original oral presentation of papers has been altered in this publication, to place together chapters with closely related subject matter. The bibliographies at the ends of the chapters, the author citation index, the subject index, and the brief notes "About the Authors" will enable the readers to make their own connections with the work presented here, and to read further into the large body of peat-related literature.

The success of the workshop is largely attributable to the skill of the organizers, and to their graciousness and good humor in coping with the difficulties and challenges of an international scientific meeting. Prof. Esteban Chornet of the Université de Sherbrooke and Dr. Ralph P. Overend of the NRCC first discussed with the editor of this volume their idea of a symposium stressing fundamental scientific aspects of peat-water relationships, and the desirability of a publication embodying the views of leading investigators in this field. Mr. Ted E. Tibbetts and Mr. John D. Sheppard, of the NRCC, capably handled the logistic and financial problems of the meeting of June 19, and of combining that meeting with the somewhat different symposium of the two preceding days.

Mr. George Olley of Elsevier Applied Science Publishers Ltd., of London has assisted the editor greatly in guiding these papers into publication.

The editor's appreciation for the individual efforts, often at great personal expense, of many of the contributors has been expressed privately. The worthwhileness of these efforts commends these papers to readers who have more than a superficial interest in peat.

PEAT AND WATER: THE UNRESOLVED PROBLEMS OF PEAT-WATER RELATIONSHIPS

The questions which motivate these chapters can be stated simply. "Why does peat retain so much water so strongly?" "How can our present understanding of the nature of peat lead us to better dewatering procedures?"

These questions are of obvious importance in peat fuel technology. They apply as well to non-fuel applications, ranging from the production of horticultural peat to the manufacture of peat-derived industrial chemicals. They are important, too, even for such"non-uses" as the preservation of natural peatlands.

Peat, in nature, contains typically 80-90% water. For fuel use it should contain less than 55% water (Mikola & Kautia, 1972). Presses and other conventional mechanical devices for dewatering peat have generally been unable to reduce the water content of fresh peat below the 70% level, although some recently introduced equipment is reported to do better (Lau et al., 1986). Commercial sieving and filtration are accompanied by substantial losses of fine particles and colloidal peat in the effluent, so that the operating expense of even this essentially mechanical operation is increased by the loss in yield, and by the disposal cost of a filtrate high in organic matter.

Water removal may be facilitated by heating the peat under conditions favoring the breakdown of the physico-chemical structures which contribute to water retention. Experimental thermal treatments differ in the temperature and duration of the heating, and in the

equipment employed (Chornet et al., 1982; Smith et al., 1986; and others). Such processes comprise "wet carbonization", i.e., an increase in the carbon content of the solid phase by heating wet peat, usually to temperatures above the boiling point of water. The use of heat to aid the dewatering process is accompanied by considerable chemical changes which are at present only partly understood. What is certain is that the chemical composition of the effluent waters is changed by the heat treatment. The treatment of such wastes to reduce environmental pollution and to obtain useful byproducts has been the subject of continuing study (Spigarelli et al., 1986).

While peat dewatering practices have developed as adjuncts of single-product commercial activities, devoted respectively to fuel peat, horticultural peat, etc., increasing consideration is being given to integrated processes, in which a variety of products are made. A possible process combination of peat wax production with coke, yeast, or fertilizer production was noted by Fuchsman (1980). Forsberg et al. (1986) has suggested that a peat chemicals industry in Canada can develop only if it is characterized by such integrated processes. This approach has been the subject of major Soviet symposia on the "complex utilization of peat", (e.g., Lishtvan, 1975). If a single dewatering procedure is to be adapted to the industrial requirements of each of several peat-derived products, a more detailed and theoretically grounded understanding is needed in the chemistry and physics of water retention in peat.

Rapid removal of water from peat appears to be difficult; but slow removal, as in the case of field drying under favorable weather conditions, occurs without great difficulty. In low rainfall years, peatlands may, in fact, become dry enough to constitute a serious fire hazard. Peat, air-dried in the laboratory for a few days, commonly contains as little as 8-10% moisture.

When the water content of peat is reduced to levels substantially below 50%, it becomes progressively more difficult to rewet the solids. Drying apparently involves changes other than the simple reversible loss of water molecules. This commonly observed loss of rewettability still lacks an adequate verifiable scientific rationale, although numerous speculative explanations have been offered.

The first stages of dewatering occur during peatland drainage, preliminary to the physical removal of peat from its natural setting. Despite an increasing volume of literature on peatland hydrology, drainage practice is mainly empirical, and does not yet appear to be extensively correlated with observations on the physical, chemical, and microbiological changes in peat during water removal.

The structure of peat, examined at the macroscopic, microscopic, and molecular levels, engages the talents of specialists from diverse scientific fields, many of which are represented in the work of the authors of this book.

Peat-water relationships can be advantageously viewed from the perspective of a geologist. The conversion of peat to lignite and coal, occurring over long time periods, is characterized by an increase

in carbon content and a loss of water. It may be of interest to learn to what extent the chemical direction of this geological change conforms to that produced in the laboratory or in the industrial plant. Can we design processes to achieve in minutes or hours the transformations produced in nature in the course of thousands and millions of years? Professor Lüttig offers a description of the sequence of changes which the organic remains of plants undergo in the process of "coalification".

Water loss, on an engineering rather than geological time-scale, is treated by Professors Edil, Bosscher, and DeWitt. Peat is viewed as a porous compressible solid mass. The variability of pore structure, the orientation of the water flow to the direction of compression, and the ways in which the stress-strain relationship changes with time are the concepts around which one can construct a model for the movement of liquid through peat.

The characteristics of water movement in ditch-drained peatland is the subject of discussion by Loxham and Burghardt. In this case the main driving forces for water removal are the hydrostatic head of water above the ditch and the weight of the peat overburden.

The retention of water by peat can be considered in terms of reactions of water molecules with the surfaces of peat particles. The phenomenon is therefore amenable to the analytical methods of colloid and surface chemistry. Professor Kwak describes some basic characteristics of a mass of wet solids in which fine particles,

fibers, capillary tubes, and voids are characteristic features. Since the surfaces of colloidally dispersed particles carry electrical charges, alterations of pH may produce aggregation, facilitating subsequent separation of the solid and liquid phases.

The retention of water in layers, sometimes only a few molecules thick, on the internal surfaces of peat particles, is profoundly affected by the hydrophilicity of the solid surface. However, water retention is also a reflection of the difficulty of aggregating colloidally dispersed peat particles. The effect of surface-active agents on improved aggregation is also discussed by Professor Kwak and his co-workers. Professor Flaig, identifies peat micropores as the principal sites for hydrogen-bonding and adsorption of water.

A somewhat different approach to water movement in peat is derivable from studies of metal-ion sorption and desorption, reviewed by Professor Kadlec. Metal ions in the liquid phase can be transported by bulk movements of the liquid, and by diffusion. The latter is important in crevices and capillaries where bulk movement of water is virtually zero. Studies of rates of ion sorption and desorption provide insights into the physical character of these interior channels in peat.

The hydrophilicity of peat surfaces is generally attributed to the availability of organic functional groups capable of hydrogen-bonding. Such groups, well-known to organic chemists, include carboxyls as well as phenolic and alcoholic hydroxyls. These oxygenated structures are present in humic and fulvic acids and in carbohydrates. The structure,

origin, and fate of such molecular configurations are thus clearly linked to the water retention properties of peat soils.

Professor Flaig's discussion of humic acids centers on the probable derivation of these substances from lignins. The complex structure of humic acid is interpreted as the result of the degradation of high-molecular weight lignin polymers, and the reaction of these degradation products with nitrogen-containing compounds, especially proteins and amino acids. This sequence of microbially mediated processes includes hydrolyses, oxidations, and condensations. Since the original lignins vary with the type of plant from which they come, the humic acids also display considerable variability in structure.

Dr. Wershaw and his colleagues offer a detailed spatial model to rationalize the water retention behavior of humic substances. Using biological membranes as analogs, they develop a structure in which the largely hydrophobic interior has a sufficient number of hydrogen-bonding sites to give the aggregate structural integrity. The outer surface, containing most of the hydrophilic groups, is mainly responsible for the retention of substantial amounts of water.

Dr. Schnitzer's description of humic acids (1982) had stressed hydrogen-bonding among aromatic carboxylic groups of smaller molecules, rather than covalently bonded configurations of high molecular weight. In this book, he addresses the question of the relationship of water to humic acids, using a variety of physical measurements. His study of surface tension, inter alia, attempts to correlate "water-sensitive" areas with hydrophilicity and the presence of oxygenated groups in the

structures of humic and fulvic acids. Electron-microscopic evidence of the shape of humic acid particles is adduced to delineate a new picture of humic acid surfaces.

The variation in the aromatic hydroxyl and methoxyl contents of humic substances should bear on the water retention characteristics of peat, since hydroxyl groups are strongly hydrophilic, whereas methoxyl groups are likely to be hydrophobic. The relative amounts of these two groups at various levels in a peat profile are traced, by Drs. Anderson and Hepburn, to the chemical contents of the plants from which the peat is derived, and to the degree of decomposition.

Dr. Hatcher and his co-workers, in studies on a subtropical peat, trace the course of humification, which they correlate with the progressive disappearance of the carbohydrate fraction of plant residues and the modification of lignins. On the basis of ^{13}C NMR studies, and other laboratory investigations, they also identify a paraffinic component, contained in the "holocellulose" fraction, which appears to be of algal origin.

Structural details of peat components have been investigated by degradative methods. In the procedure used by Dr. Boon and his colleagues whole peat samples are rapidly pyrolyzed at 510°C, and the pyrolysis fragments analyzed by GC-MS techniques. The resulting spectrograms exhibit patterns of abundance characteristic for each of the different types of starting materials. They can be used to identify the relative amounts of carbohydrates, lignins, etc. in the sample, and thereby establish the plant origin and the degree of

decomposition of the peat. Fragmentation patterns are correlated with botanical observation and can thus provide a history of the peat profiles.

The work of Hänninen and his fellow researchers in Joensuu, Finland has been directed to the elucidation of peat humic acid structure by controlled chemical degradation. The classical problem in the use of chemical methods to determine the structure of high-molecular weight compounds is the selection of degradation techniques mild enough to yield identifiable products which still retain essential elements of the original complex configuration. If the degradation is too harsh, the product molecules are too simple to be informative; if it is too mild, the inner structure remains inaccessible. The Joensuu chemists have used alkaline cupric oxide as an oxidizing agent to obtain a variety of aromatic and aliphatic products representative of parts of the humic acid molecule.

Although the microorganisms in the soil are generally acknowledged to have a major role in humification, it has not always been possible to identify particular products as those of microbial metabolism. It is hard to rationalize the growth and survival of such living forms in peat, where conditions appear to be adverse to many essential biochemical processes. The heterotrophic organisms of the soil, those which must ingest carbohydrates and amino acids to meet their metabolic needs, secrete enzymes into their surroundings to catalyze the solution, usually by hydrolysis, of dead plant matter. These enzymes are all proteins, and are thus subject to hydrolysis, and to being

otherwise denatured or inactivated by adsorption onto humic acids or clay particles. Nevertheless, it is possible to extract enzymes from soils and to demonstrate their activity. Since the enzymes are involved in the breakdown of substances which promote water retention in soils, their mode of existence becomes important in an account of soil-water relationships. Professor Mayaudon has investigated such an enzyme, and described a sequence of reactions by which it is protected in an environment that would otherwise destroy it.

While humic acids have been regarded as the component principally responsible for water retention in peat, carbohydrates also play a significant part. In addition to cellulose and a variety of non-cellulosic carbohydrates which are bequeathed to the soil by the death of higher plants, complex polysaccharides, lipopolysaccharides, glycopeptides, etc. are synthesized by bacteria and fungi. The hydrophilicity of these substances depends not only on the numbers of hydroxyl and other polar groups, but on the type of bonding of their monomer units. Sugar units linked in one way may expose their free hydroxyls to hydrogen-bonding with water; but linked differently may become relatively inaccessible to water. Professor Gander and his co-workers report in studies the structure of a polysaccharide synthesized by Penicillium, a genus of fungus found in peats and other soils.

The chapters (of the book) which follow develop in some detail these areas of investigation, important to improvements in peat technology.

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PEAT AND WATER: THE PEAT-WATER PROBLEM - REFLECTIONS; PERSPECTIVES; RECOMMENDATIONS*

There is considerable merit in assembling the views on peat chemistry, physics, and microbiology, of authors with diverse special interests. While no all-embracing self-consistent theory relating peat structure to water retention emerged from the meeting of these scientists at Rivière-du-Loup, a synthesis of many of their ideas now seems much closer. The technical questions to be addressed are more clearly definable and, within the scope of presently available techniques, should be answerable by the scientific community.

The rich variety of ideas brought together here is reflected in the publications cited by the contributors to this book. Each contributor offers not only his own recent findings, but the important ideas of predecessors and contemporaries. Seeking the unifying concepts that link such diverse efforts is both stimulating and necessary. The reader is encouraged to browse through the Index of Author Citations and make his own useful connections.

The retention of water by peat can be usefully viewed from several vantage points. It can be seen as a factor in geological transformation over the course of a few thousand years, as in bog formation; or over millions of years, as in the evolution of coal. In

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*Where no dates are given for citations of work by contributors to this book, the reader is referred to their chapters.

each case the retention of water is both an evidence of the state of geological change, and a factor influencing subsequent change. Peat-water relationships are also critical elements in engineering design calculations for field drainage and for commercial filtration. The alteration of peat's affinity for water, by thermal, mechanical, or chemical treatment, has been extensively studied. The results are promising. Water retention has also been examined as a problem in hydrology, where the rate of liquid flow is largely determined by the network geometry of micropores in peat. Several contributors to this book have attempted to provide a means of predicting, from simple measurements of peat structure, the course of drainage and filtration.

Considerable attention has been paid to the chemical composition of peat, identifying the molecular characteristics of substances and aggregates most likely to hold water strongly. Knowledge of these structures can provide a rationale for treatments intended to remove, or render less water-retentive, the most hydrophilic fractions. The substances of greatest immediate interest are humic acids and carbohydrates, and new information is provided here on their chemical compositions. The techniques for the study of these substances range from those of biochemistry and classical organic chemistry to gas chromatography, mass spectrometry, Curie-point flash pyrolysis, and isotopic labelling. Advanced mathematical and computer-based analyses have generated valuable data from minute samples, without the need of extensive prior fractionation of mixtures.

(a) The geological perspective

Peat, as Prof. Lüttig reminds us, is a stage in coal formation. The overall process involves a gradual carbon-enrichment of the organic portion, with a corresponding diminution of oxygen and, more slowly, of hydrogen. The advantage of coal as a fuel, compared with peat or with the plant material from which the peat is derived lies, in large part, in the reduction in the oxygen content of the organic solid phase.

The process of coalification is not inexorable. The process may be halted by man, or by environmental conditions, at various points along the path. Some very old coal deposits have lower carbon contents than others of more recent origin.

The process is therefore not simply a function of time. Other conditions, including the presence of some inorganic mineral substances, affect the rate and extent of transformation. High temperatures and pressures are known to accelerate the change.

The access of water to peat is dependent on rainfall and on groundwater movement. Climatic changes from dry conditions favoring ericaceous peats, to wet conditions favoring Sphagnum moss peats, have been described by Dr. Boon and his co-workers. Dr. Boon's data are obtained by using advanced pyrolysis-gas chromatography-mass spectrometry techniques. Sphagnum peats have high polysaccharide contents, while ericaceous peats have more lignin and/or humic acids. Since the polysaccharides have, in general, a greater tendency to retain water than do the more aromatic lignins and humic acids, the causal association of water and carbohydrates in peats seems to be

reciprocal. In other words, wetness fosters the development of plants whose chemical components are highly water-retentive.

The process of conversion of decaying plants to peat and coal is one of continual loss of carbon, as gaseous and soluble organic byproducts of decomposition. Fossil solid fuels (caustobioliths, as Potonié called them) constitute only a small fraction of the amount of carbon originally present in the living plants from which the peat and coal were formed.

Modern efforts to dewater peat find analogs in geological processes. The alteration of surface drainage patterns by earth movements, resulting in water loss and increased aeration, finds its parallel in ditched peatland drainage. The geological counterparts of thermal dewatering have their parallel in "wet carbonization" and coking processes.

Whether the later stages of coalification represent a continuation of the chemical processes of peat formation, or a different category of chemical change, is unclear. During peat formation, the carbon content of the organic residue is increased (when compared to that of plants). In this sense peat formation is part of the continuum which leads to coal. The water content of peat, however, follows a different course. Peat attains an affinity for water which is apparently greater than that of either plants or coal. Water contents, at 80-90% of the weight of undrained peat, mark the culmination in the development of water-retentive structures and substances. Peat constitutes the stage at which the processes which generate hydrophilic sites reach their

maximum, and are gradually superseded by those which replace hydrophilic by hydrophobic groups.

The surficial geology of peats has not yet provided an adequate data base from which to estimate the comparative feasibility of alternative dewatering processes. Preliminary studies on the chemical mapping of peat (Pihlaja et al., 1984) may point the way to identifying the pertinent compositional and physical properties needed in stratigraphic soil maps of peatlands. Data on bitumen, humic acid, and carbohydrate contents, along with estimates of porosity and hydraulic conductivity would certainly be useful in interpreting peat surveys, and in designing peat dewatering processess.

Dewatering by drainage irreversibly alters the peat transformation sequence so that coalification in the geological sense becomes less relevant. Drainage means that air replaces water in the interstices among the peat solids. The aerated peat solids evolve along pathways which differ radically from those of wet unaerated peat. On exposure to air, unharvested peat loses carbon, primarily as carbon dioxide. If the soil is converted to agricultural or forestry use, the losses in organic matter are largely balanced by the die-off of leaves and annual plants, but the cycle of change no longer resembles that of peat, either with respect to water retention or with respect to the molecular composition of the organic fraction.

(b) Alternatives to drainage of peatlands.

Drainage of bogs is a common first step in the exploitation of peat for fuel or horticultural use. Alternatives to drainage exist,

and have been used on a commercial scale. Thus, in hydraulic mining, peat is transferred as a dilute suspension to equipment which removes coarse ingredients (e.g., large roots), and then filters the mixture (Carncross, 1984). The filtered product, which still contains 3 parts of water to 1 part of solids, requires further drying for fuel use. In view of high shipping costs, supplementary drying is also desirable for such peat sent to the horticultural market.

Another alternative to conventional drainage is the harvesting of peat as a slurry to be fed to a wet carbonization process. Following heating, with its attendant chemical changes, pressure filtration of the solids yields solids with as little as 50% moisture (Rohrer, 1982). This filtered product can be used as fuel.

Both wet carbonization and hydraulic mining are handicapped by the passage of substantial amounts of solids through the filter presses into the filtrate. The amount thus lost varies with operating conditions but is typically 20-25%. This loss of organic material is reflected in reduced product yield and in increased waste disposal costs. Recycling of liquid in hydraulic mining operations, and the use of large settling basins, can reduce the quantity of suspended solids in the plant effluent. In wet carbonization, however, much of the increased organic content of the wastewater is colloidal or soluble, and thus not easily recovered. There are also difficulties in meeting effluent water quality standards, since the discharge liquors are not readily purified by conventional microbiological treatments. Studies of such treatment have been reported (Spigarelli et al., 1986).

However, a comprehensive investigation of the microbial treatment of effluent from wet carbonization processes is clearly needed, if serious water pollution problems are to be avoided. An attractive possibility is the use of at least part of the organic substance in the effluent as feedstock for the cultivation of yeasts, or other heterotrophic microorganisms to produce single-cell protein for consumption by livestock or humans. In such cases the disposal cost may be more than offset by the value of the by-products.

The possibility of combining a peat dewatering operation with the biotechnological production of alcohol or protein, illustrates a recurrent theme in the contemporary discussion of peat problems: the integration of peat processes to maximize overall revenues, and to minimize unit costs.

(c) Drainage as a means of dewatering peat.

Peatlands may be drained for several purposes. The drained peat may subseqently be removed for horticultural use; or, as is often the case in Finland and the Soviet Union, drainage is preparation for afforestation on the peat soils (Heikurainen, 1983). Field drainage of peat, when properly designed, may not significantly alter the quality of the effluent waters (Korpijaakko and Pheeney, 1976), in part, because the relatively undisturbed peat acts as an efficient filtering medium for the outflow. However, peatland drainage is slow, usually requiring months to years before peat can be removed as sods or milled product. The peat after drainage is still too wet for fuel use and is usually windrowed and air-dried, a procedure which makes peat

production weather-dependent. The optimization of field-drying of peat has been the subject of several studies (e.g., Ivanov et al., 1983). Many years of practical experience permit rough predictions of drainage rates, and of accompanying shrinkage and subsidence. A sound theoretical basis for such estimates has been lacking. Attempts have now been made to provide more sophisticated tools for such predictions. Prof. Edil and his colleagues have constructed a computerized hydrological model for peatland drainage, and have applied it successfully to changes in piezometric heads in a bog where outflow rates exceeded inflow from several springs.

Loxham and Burghardt have analyzed gravity drainage of peat in terms of flow through a complex pore system. The pores are created by the plant residues and consist of large channels (macropores) and small ones (micropores). While about 85% of the typical saturated peat was occupied by the liquid phase, only about 15% of the total volume, or about 18% of the pore volume, is hydrodynamically active (Loxham and Burghardt, 1984). The inactive space consists of very fine pores (<30 μm in diameter) and larger pores which are not connected to open-ended channels. In the course of drainage, the macropores are soon emptied; or, because of their lack of adequate connection to one another, cease to serve as conduits for the effluent waters.

In saturated, i.e., partially drained peats, larger pores are no longer significant. Loxham and Burghardt, in their current work, include the effects of the cross-sectional shape of the remaining microporous channels in their calculations of the overall flow rate.

Micropore interconnections and tortuosity affect the rates of discharge of water. Unlike the macropores which shrink significantly as drainage proceeds, the micropores retain their dimensions largely unchanged as the water is removed, until in the late stages, they deform slightly. Confirming field experience, the authors find that hydraulic permeability drops by several orders of magnitude as unsaturation increases. The analysis, expressed in terms of the equations of hydrodynamics, leads to reasonable predictions of water flow in some German bogs. It is however evident that additional work is needed to attain predictability of flow over a wide range of conditons and peat types.

(d) High stress mechanical dewatering.

Gravity drainage is slow. It depends for its driving force, on the weight of the wet peat lying above the ditch water level. Because of capillarity and related surface phenomena, the effect of the peat weight on water removal diminishes rapidly with distance from the drainage canals. To overcome these disadvantages engineers have designed equipment which generate enormous stresses intended to collapse the pore-system and thereby to expel peat water.

Commonly, in commercial filtration of peat slurries, after removal of coarse undecomposed plant fragments, one obtains a solid filter cake containing about 70% water, or about 2 parts of water per part of solids. Since undrained peat typically contains about 8 parts of water per part of solids, it appears that about three-fourths of the water is readily removed by conventional mechanical means. Presumably this

easily removed water is initially present in large channels and macropores.

Edil and his co-workers report on studies of the effects of high-pressure filtration in laterally constrained peat samples. Compressive forces, applied to wet peat, generate complex strains and flow patterns. Some water is expelled quickly, as the peat sample is compacted. This reduction in volume increases the resistance to further liquid flow. Filtrate is produced at diminishing rates as the physical matrix of peat solids accommodates to the pressure. If there is no increment of externally applied pressure, the internal pressure in the system slowly diminishes. Pressure applied at constant strain (i.e., at constant rate of diminution in volume) increases rapidly, especially in highly compacted peat. But even at the higher pressures, with water outflow diminished to a low level, the sample contains more water than is acceptable for fuel use.

Such compressed samples rapidly become anisotropic. The permeability in horizontal directions (i.e., perpendicular to that of the applied stress) is several orders of magnitude greater than it is in the vertical direction (i.e., parallel to the applied stress).

It seems likely that the coarse channels are crushed and the 3-dimension sponge is reduced to the equivalent of a flat felt mat. The deformation of the channel structure of peat is not instantaneous. The stress applied to the peat causes a high initial strain which gradually diminishes as water is lost and the peat structure is compressed. Analysis of strain and water release as a function of time

confirms the complexity of the process. The slow continued loss of water reflects the continued accommodation of the solids to internal stresses. Test data indicate that the residual water in the compressed solids is approximately the same as that generally reported in the literature for pressure-filtered peat. About one to two parts of water per part of peat solids represents an apparent limit for the rapid mechanical dewatering of peat. Water removal beyond this limit appears to require radical alteration of the solid phase, or evaporation.

Further improvement may result from the use of shear forces, as Prof. Kwak has suggested, to break down the solid structure further and free trapped or occluded water. Such a mechanism may be involved in a system in which peat is squeezed in the nip between two cylinders, one interior to the other, particularly if the cylinders rotate at different linear speeds. Moisture contents of peat filtered by such equipment may fall below the maximum allowable levels for peat fuel (Lau, 1986). This procedure however appears to be accompanied by substantial loss of finely divided solid peat in the effluent, a characteristic of almost all commercial filtration sytems.

It is desirable to extend the investigation of systems which combine compression and shear to improve dewatering of peat, and to devise methods for the recovery or use of finely divided solids in the effluent of such pressure filters.

(e) <u>The physical chemistry of peat surfaces.</u>

The structure of peat cannot be described simply, in part because of the wide range of forms to be found among peat particles. Water retention by this heterogeneously-structured system depends on the

chemical nature of the solid surfaces. These naturally wet solids, if dried sufficiently, lose the ability to rewet quickly when immersed in water. This widely noted phenomenon is not yet adequately explicable in terms of observed chemical changes.

The ability of peat surfaces to attract and hold water is attributed to hydrophilic functional groups which characterize the organic substance of peat. These groups are generally oxygenated, mainly phenolic and alcoholic hydroxyls, and carboxyls; or nitrogenous, usually amines, amides, and N-bearing heterocycles. Such groups can hydrogen-bond with water molecules.

Peat particles are thus coated with stable water films whose thickness varies from one to several molecular layers. The geometry of these water-attracting surfaces is of some importance in devising methods for water removal. Professor Flaig has observed spheroidal particles in chernozem humic acids with diameters up to 100Å. Dr. Schnitzer has now reported on podzol humic acids and fulvic acids in the form of extremely fine fibers. Although it is widely assumed that humic acids from chernozems and podzols are similar to those from peat soils, it is possible that differences in origin, or in the methods of sample preparation, may account for the observed differences in geometric form. While both products have very large surface:volume ratios, the more elongate fibrous forms observed by Dr. Schnitzer suggest a different spacing of polarized atoms in the humic acids, and possible differences in the mass of the individual molecules, when compared with those of Professor Flaig's spheroidal aggregates (Flaig et al., 1975)

Both these geometric forms can attract and hold water at their surfaces in a molecular layer (the electrical double-layer), and in the immediate vicinity (the Stern layer). Prof. Chornet (University of Sherbrooke) noted, in discussion of these papers, the importance of these large surfaces. If the surface:volume ratio is large enough in the humic acid particle, a considerable portion of the observed water retention in peat can be accounted for.

Since some of the hydrophilic groups, especially the carboxyls, ionize at naturally occurring pH conditions, the surfaces are also likely to be electrostatically charged. The charges, mainly negative, repel neighboring peat particles, thereby resisting compaction, and increasing the difficulty of expelling water from the intervening spaces. These charges can be overcome by the addition of cationic surfactants, although at present the quantities of surfactant required are uneconomically large for use as commercial filtration additives.

Water-wettable surfaces in the forms of capillaries or crevices, are capable of holding water at distances considerably greater than the thickness of a few molecules. Such water cannot easily be expelled mechanically. The cracks and tubules may exist in the coarse structure of the peat; but, as Professor Kwak pointed out in oral discussion of the subject, no special structures are required to produce the phenomenon of capillary retention of water. The mere juxtaposition of peat particles creates the necessary small spaces.

The shape of the peat particles in the water retention system can affect mechanical dewatering in other ways. In the case of spheroidal

particles the water in the interstices can be expressed by deformation of the spheres. With the fibrous particles reported by Dr. Schnitzer, a parallel orientation of the solids would permit denser packing, and therefore smaller overall volume. The design of mechanical equipment intended to dewater an aqueous dispersion of humic substances would thus be influenced by data on the shape of the particles.

Dr. Schnitzer's observation that humic substances, which constitute significant fractions of most peats, may exist in the form of extremely fine fibers, should encourage further study of the surface properties of the components of native peats. It would be of great interest to know to what extent the particle shapes observed in humic substances regenerated by solution and reprecipitation correspond to the forms occurring in untreated peat.

(f) Humic acids and other humic substances

The chemistry of soil organic substances has been the subject of intensified study in the last 30 years, as newer and more refined analytical techniques have become available. Difficulties inherent in the heterogeneity of these substances still preclude adequate descriptions of the humic fractions of the soil, and obscure the processes by which they are formed. The death of higher plants is accompanied by the slow and uneven breakdown of tissues and cells. Some plant structures, especially plant fibers, persist in recognizable form even in highly decomposed peat, while softer parts seem to disappear rapidly. With the breakdown of plant tissues there appears an increasing quantity of soft dark-colored amorphous particles, which are identified as humic substances. The amount of non-fibrous material

in peat is commonly considered a measure of the "degree of decomposition". Many methods have been developed to obtain reproducible quantitative estimates of the degree of decomposition, but all such methods are arbitrary. Weak fibers, if sufficiently fragmented, will be accounted as humic substances, along with any non-fibrous materials from higher plants. On the other hand, decay products occluded in the plant fibers are reported as part of the non-humic fraction. One of the merits of Dr. Boon's pyrolysis studies lies in the ability to identify undecomposed plant substances even where the original plant structure is no longer visible under the microscope.

Humic acids, comprising one fraction of the humic substances, are defined by their solubility in alkali and by their ability to be reprecipitated by mineral acids. They are known to possess carboxyl groups. Although they differ significantly from the principal components of higher plants, the presence of phenolic hydroxyl groups has suggested to many investigators that humic acids are derived from lignin.

The presence of carboxyl and phenolic hydroxyl groups can account for the hydrophilic nature of humic acids and their importance in peat-water relationships. Nevertheless the physical distribution of humic acids among the microscopically visible structures in native peat remains unknown. Study of that distribution would help clarify the mechanism by which peat retains water, and would therefore rationalize the further study of dewatering processes. If humic acids are generally distributed as matrix material or as coatings of non-humic

particles, then it will be impossible to separate these acids by mechanical means, (i.e., by methods based on differences in particle size or shape, in density, or in hardness). If, on the other hand, humic acids are highly concentrated in some particles, physical separation methods may make dewatering more efficient.

The feasibility of physical separation processess may be evaluated by the further study of high pressure filtration to yield relatively dry filter cakes. The large losses of fine particulate matter into the filtrate should be examined for humic acid content. Is humic acid more highly concentrated in the effluent solids than in the filter cake?

The inner structure of the humic particle may account for its colloidal character. It is useful to know what gives such particles their stability. If, as usually conceived, these particles have a high enough concentration of identical ionic charges on their surfaces to repel nearby particles, there must be similar electrostatic repulsions among these surface charges to cause the particles to disintegrate. Since the particles are stable, various cohesive attractive forces are postulated. If the humic acid molecule is large the charged particle may be held together by its covalent bonds. This model accommodates the view of humic acid as a modified lignin, described by Nimz (1974), and referred to in Professor Flaig's chapter.

However, a long standing view of humic acids attributable to Odén (1922), gives a molecular weight of about 1350, and equivalent weights of about 340. Since particle weights from about 3400 to about 91,000 have been reported by various investigators (Fuchsman, 1980, p. 146), humic acid particles appeared to represent aggregates of 3 or 4 to about 100 molecules.

Dr. Wershaw, however, offers a model of humic acid structure which substantially alters the concept of micellar aggregation of small humic acid molecules. His proposed structure, which is not limited in geometric shape or size has a characteristically hydrophilic exterior surface, and a hydrophobic interior.

In his earlier work, Wershaw had shown that Sephadex fractionation of humic acids yields products which are chemically dissimilar, and which exhibit different aggregation responses to pH change. One fraction strongly displays, in ^{13}C NMR spectra, typical carbohydrate characteristics while other fractions appear to be phenolic and aromatic carboxylic acids, suggestive of lignins and tannins. These fractions may presumably be combined in a variety of ways to yield elongate, layered, or globular structures. Wershaw's model is extended also to humins, the humic substances which are not extractable with acid or base, but which are appreciably soluble in methyl isobutyl ketone following the method of Allen et al. (cited by Wershaw). Humins appear to contain more aliphatic and less aromatic structure than do humic acids.

This model could explain the appearance of water-soluble "fulvic acids" when humic acids are dissolved and reprecipitated. The appearance of "fulvic acids" in the course of analysis for peat humic acids had always been puzzling. This "water-soluble fraction", which contains significant quantities of carbohydrates (Fuchsman, 1984), does not appear to be water-extractable from untreated peat. However on solution of humic acids in dilute alkali, the fulvic acids appear, and remain in solution when the humic acids are reprecipitated by treatment

with acid. From Dr. Wershaw's model it appears that these water-soluable materials may be loosely held by hydrogen-bonding to humic acid molecules in naturally occurring aggregates. The fulvic acids may have been held within the hydrogen-bonded "membrane" structure in nature. The breakdown of this complex structure by the addition of alkali releases occluded water-soluble compounds which remain in solution when the humic acids are reprecipitated. The reprecipitated acids are thus purified and denatured. The Wershaw model implies that the physical properties of natural humic acids, including those concerned with water retention, are likely to be substantially different from those of the solids recovered by the conventional solution-precipitation procedure. It is, of course, the reprecipitated humic acids which are used in modern chemical studies of structure.

The pyrolysis of Dr. Boon and his co-workers may be particularly pertinent to the "membrane model". Boon's discriminant function distinguishes between the highly aromatic fragment pattern obtained in ericaceous peats from the more typically carbohydrate-derived pattern observed in the case of Sphagnum peat. Wershaw's model can accommodate an oxygenated aromatic outer surface, with carbohydrates occluded in the interior. Variable discriminant functions may simply correspond to variable levels of carbohydrate occlusion.

Dr. Wershaw emphasized the hydrophobic character of the interior of the humic acid "membrane", and the hydrophilic nature of its exterior. However the heterogeneity of the structure provides ample

possibility for water-containing spaces within the overall configuration. The water in such a mechanically stable structure would be difficult to remove.

(g) The chemical composition of humic acids.

Humic acids, obtained by reprecipitation with acid from alkaline solutions of humates have been studied extensively. The conceptual framework within which chemical investigations have been conducted is conditioned by theories of the origin of humic substances. The most widely accepted view appears to be that humic acids are chemical derivatives of lignin. This view, discussed by Prof. Flaig at the Rivière-du-Loup meeting had been developed in some detail in an earlier publication (Flaig et al., 1975). It is the view which underlies Dr. Hatcher's picture of humification of Florida peats.

The rationale for the lignin origin is partly based on the observation that, apart from the persistent cellulosic fibers, the large carbohydrate component of living plants is readily attacked by the microorganisms of decay, while the lignin fraction is more resistant. Lignin is now known to be a heteropolymer in which the principal monomeric units are 2-methoxy (or 2,6-dimethoxy) phenols with an oxygenated three-carbon chain substituted in the 4-position. Apparently microbial demethylation of the methoxy groups occurs quickly, but further attack by microorganisms is slow. Various mechanisms have been proposed for the conversion of demethylated lignins to humic acids.

The basic difficulty in analyzing humic acids and lignins by the classical methods of organic chemistry lies in the need to break down a

polymeric structure into fragments small enough to be identifiable, yet large enough to be informative about the original structure. Oxidative degradation under severe conditions usually yields only carbon dioxide and low-molecular weight organic acids. Under mild conditions little useful reaction occurs.

Anderson and Hepburn have used 3,4-dihydroxybenzoic acid as a chemical indicator of the degree of conversion of lignin to humic acids in fen and hill peats. The compound, which appears in the acid hydrolysate of peat humic acids, is the hydroxylation product of p-hydroxyphenyl lignin moieties, or the demethylation product of a guaiacyl lignin. The trimethylsilylated derivatives of the dihydroxy acid and of its precursors are individually measurable by gas chromatography.

Chemical degradation methods which appear to be suitable for structure determination work have been used in recent years in Spain and Finland. In Spain Martin et al., (1981) have used acid persulfate degradation techniques, while in Finland, Hänninen and his coworkers have used alkaline cupric oxide oxidation. The latter technique has now been used to estimate lignin in the presence of humic acids. Lignin was found to constitute only a small fraction of a sample of Finnish peat humic acid. Earlier work had shown that, on analysis of peat derived from Sphagnum moss, no typical lignin oxidation products are found, presumably because the living moss contains no true lignin.

Of particular interest in Hänninen's report is the presence of large amounts of long-chain aliphatic mono- and di-carboxylic acids

among the oxidized products of humic acids. Since such materials cannot originate from lignin, the general view that humic acids are primarily lignin degradation products must be reconsidered.

Dr. Hatcher and his colleagues also encountered substantial amounts of aliphatic material, which they attributed to the presence of algae in Florida sawgrass peats. A further explanation of the seemingly low level of aromatic substances in the peat, offered by Dr. Hatcher, and by Dr. Anderson, is the likelihood that the humic acids form soluble complexes which then migrate from the peat through the groundwater system. Measurement of the solubility and diffusion rates of humic acids and their metal complexes at various pH values would contribute significantly to a picture of the mobility of humic acids in peat.

(h) The role of metal ions in peat.

Within the micropores, or in interstitial spaces of Professor Kadlec's model of peat, the movement of metal ions may have many implications for peat-water relationships. In the smallest spaces, bulk transport is slow and the diffusion of ions and water molecules becomes correspondingly more important. But in such spaces the adsorption or desorption of large metal ions may substantially alter the effective shape and dimensions of the channels. The presence of metal ions affects the contour of the static hydration layer on the pore walls, and by changing the distribution of ionic charges, may strengthen or weaken the channel to compressive forces. Thus the manipulation of metal ion concentrations, and of pH may be useful ways to increase the effectiveness of mechanical dewatering of peat.

Metal ion adsorption on peat also has implications for biochemical and microbiological investigations of peat-water relationships. The organic materials associated with water retention in peat are subject to enzyme-mediated degradation. The vulnerability of peat to microbial attack may be reduced by the presence of appropriate metal ions. The loss of organic matter in drained peatlands by subsidence can be retarded by the addition of copper salts (Mathur and Sanderson, 1980; Mathur, 1982 and 1983). The copper apparently inactivates important enzymes produced by peat microorganisms. In enzymatic or microbiological studies of peat dewatering, it may be appropriate to consider controlled variation of heavy metal ion concentrations.

Adsorption of ions in peat is complex from both the physical and chemical viewpoints. The kinetics of sorption-desorption processes are affected by concentration gradients within the interstices of the peat particles, and, as Professor Kadlec points out, by the nature of the ions, (e.g., H^+, Ca^{++}, or Cu^{++}) occupying the sorption sites.

These active sites exhibit great chemical differences. Not all these variants have been studied. In addition to isolated carboxyl groups, where simple ion exchange reactions may occur, some sites may have adjacent phenolic and carboxyl groups which offer possibilities of stronger bonding by chelation. Nitrogen, both in amines and in heterocyclic form, may form stable complexes with transition metals.

The hysteresis effect, that is, the lack of simple reversibility of the sorption-desorption curves, thus finds its origins in many phenomena, among which are the diffusion controlled movement of ions in remote confined regions of peat particles, and the formation of chelates and of nitrogen complexes at some humic acid sites.

Prof. Kadlec has developed a mathematical treatment for the movement of metal ions in peat. Since peat is sometimes used to scavenge heavy metals from industrial wastes and other polluted waters, it is of some interest to know whether the water removed from such peats will be heavily polluted.

Kadlec and Keoleian found that the metals adsorbed on the peat exist in equilibrium with the metals in solution. The studies on adsorption-desorption phenomena with transition metals are usually made at concentrations high enough to allow observation of easily desorbable ions. However, it is likely that the metal ions are held at the humic acid surface by several different types of bonding, and that different equilibria exist, corresponding to the variety of bonds. Prof. Kadlec has distinguished between simple displacement of carboxylic hydrogen by the metal equivalent, and chelation involving adjacent carboxylic and phenolic hydroxyl groups. Transition metal complexes with amine and with heterocyclic nitrogen atoms have received less attention.

Since peat colloids are predominantly negatively charged, metal salts may be used directly to neutralize and precipitate them. Such applications could be attempted before pressure filtration, and in order to obtain drier filter cakes. One could also add metal salts to peat filtrates to aggregate the dispersed solids prior to concentration by settling, secondary, filtration, or centrifugation.

The effect of deliberate, accidental, or natural additions of metal ions to peat on dewatering characteristics merits extended study.

(i) The humin question.

Dr. Hatcher and his group have contributed to our understanding of the "humin" fraction. The humins have always been awkward to characterize, since they are usually defined as the undissolved organic residue following alkali treatment to dissolve humic acids. In peats which are not highly decomposed, the humins invariably contain fragments of the tissues of higher plants. In minerotrophic peats which are not first treated with hydrochloric acid to remove di- and trivalent cations, the humins may also contain metal humates, as Dr. Schnitzer (1982) has suggested. In addition to these fractions, humins also undoubtedly contain some high-molecular weight relatively non-acidic components resulting from the processes of plant decay.

Dr. Hatcher points out that humins as normally determined include carbohydrates, so that it is no longer valid to add the humin fraction to the separately determined "holocellulose" fraction in computing the analysis of peat.

Although the carbohydrate content of humins decreases with depth in a sawgrass peat deposit, the humins remain more highly oxygenated than the humic acids. The hydrophilic surfaces of humins are thus available for hydrogen-bonding, and may contribute significantly to water retention in peat.

It is not a large step from the humins to carbohydrates as major factors in peat-water relationships. We have, perhaps, come full circle from dismissing the carbohydrates as a quickly disappearing component in the humification process, to observing that carbohydrates

appear (as reducing agents) in the fulvic acids of degraded peats (Anderson et al., 1977; Wershaw et al., 1981; Fuchsman, 1984), to developing, in Dr. Wershaw's membrane model, a means of occluding water and carbohydrates in the predominant hydrophobic interior of humic acid aggregation.

It is desirable to correlate water-retention by peat under controlled conditions of temperature, pressure, and pH, with a variety of compositional variables, (e.g. porosity, particle size distribution, etc.). Since the separation of components denatures peat, such a study is best conducted on fresh peat using "analysis of variance" and other appropriate statistical methods.

(j) Carbohydrates.

As long as carbohydrate analysis of peat remains limited to the determination of cellulose, and the measurement of non-cellulose carbohydrates as reducing substances, or as monosaccharides following acid hydrolysis, the nature of the affinity of peat for water will probably continue to be obscure.

Cellulose itself illustrates the point. This material, which comprises much of the cell wall and fiber encountered in peat studies, is not particularly water absorbent. Despite an enormous array of hydroxyls, the crystalline ordering in this polymer permits few of those groups to extend into the surrounding aqueous medium. Most of the hydroxyls are internally hydrogen-bonded to one another. Nevertheless when cellulose is hydrolyzed, its constituent glucose monomers are water soluble, form thick syrups, and otherwise give strong evidence of solvation and bonding to adjacent water molecules.

Starch, which is also a polymer of glucose, when released from its granules into water, usually by boiling, hydrates immediately. In starch, the glucose units are not hydrogen-bonded exclusively to one another. Hydroxyl groups are available for bonding with water molecules. Starch, however, is not normally encountered in peat, but many other polysaccharides are. These polysaccharides are composed of a variety of sugar moieties: glucose, galactose, and mannose among the hexoses; xylose, arabinose, and ribose among the pentoses; glucuronic and galacturonic acids; and occasionally less common sugars such as rhamnose and fucose. These sugars and the polymers of which they are a part are not simply undecomposed residues of dead higher plants. Much, perhaps most of the peat carbohydrates are products of microbial synthesis. The evidence lies in the nature of the polysaccharides.

Peat carbohydrates are generally richer in mannose than are the carbohydrates of higher plants. While this condition could result from the more rapid consumption of other hexoses by soil microorganisms, the linkage between mannose units cannot be explained in this manner. As Prof. Gander has noted in his work on the glycopeptides of Penicillium, the mannose units are linked "1,2" (i.e., carbon no. 1 of the mannose unit is linked, through oxygen to carbon no. 2 of the next mannose unit), whereas in higher plants such linkages are likely to be 1,4. The 1,2 linkage is distinctive for yeast and fungi (Gander, personal communication).

From such observations one can ascertain the origin of the carbohydrates, and the role of carbohydrates in water retention in peat. Mannans (i.e., chains of mannose units), with 1,2-linkage offer less exposure of hydroxyl units to surrounding water than do those with 1,4-linkage.

Microbial action can thus be related to changes in water retention. However, the study of monomer linkage in hydrophilic polymers must be extended to other carbohydrates, to polypeptides, and to other peat ingredients before the overall effects of microbial activity on water retention can be estimated.

The new biochemistry alters the traditional view that carbohydrates originate in higher plants and diminish in quantity as the dead plants decompose. In fact, in the continuously changing peat composition, microbial synthesis of new carbohydrates partly replaces those consumed as food by the same microorganisms. Not only do the new carbohydrates differ in chemical composition from those which are being replaced; they differ also in physical form. The visible cellulosic fibers of higher plants are no longer to be seen in the organic matrix populated by microscopic organisms, although cellulose is still a principal ingredient of cell walls. The measurement of fiber content in peat as an indication of cellulose content becomes increasingly unreliable as the peat becomes further "decomposed"; and the chemical measurement of cellulose itself is no longer a unique indicator of taxonomic origin.

Peat colloids, too, may require reconsideration in the light of soil microbiology. They may not, after all, be simply random aggregates of molecules of "humic substances". Bacterial cells and fungal spores may behave as colloidal particles in their natural environment.

The examination of peat carbohydrates in terms of their possible microbial origin is likely to be fruitful for the development of new commercial processes for utilizing peat, as well as for insight into water retention phenomena.

(k) Nitrogen in peat.

The role of humic nitrogen in water retention does not yet appear to have attracted much attention. Professor Flaig's observation that nitrogen-containing parts of humic acid structures are more highly hydrated, despite their lower void space, should encourage further study of the nitrogen in peat.

Dr. Boon's pyrolysis mass spectra include many odd-numbered peaks attributed to nitrogen-containing compounds. The peaks appear to be more prominent in more highly humified peats. This observation supports the view that nitrogenous compounds play essential roles in humification.

Nitrogen plays a fundamental role in all life processes, and therefore in the biochemical cycling of organic compounds in peat. Its direct role in the course of water movement in peat appears to be limited to three basic phenomena: 1) Nitrogen atoms, particularly in amines and in heterocycles, can form hydrogen-bonding sites.

2) Nitrogen atoms can serve as sites for the complexation of metal ions. 3) Quaternary nitrogen compounds carry positive charges which can alter the behaviour of predominantly negatively charged peat colloids.

Prof. Kwak has reported on the use of quaternary ammonium compounds as cationic surfactants in altering the colloidal properties, and hence the dewatering possibilities of peat. Prof. Gander has described the structure of glycopeptides produced by Penicillium, a genus of fungi widely distributed in peat soils, wherein choline and ethanolamine appear as structural units covalently bonded to the polysaccharide chain. Choline, which has the quaternary nitrogen structural characteristics of cationic surfactants, appears to be common in plants, reaching levels as high as 6.4% in some yeasts (Karrer, 1958). Ethanolamine is a metabolic precursor of choline. Some carbohydrates thus not only affect water retention through direct hydration, but they also may have the potential of shrinking water-retaining spaces between large molecules by changing the ionic charge pattern on adjacent colloidal particles.

The nitrogen chemistry of carbohydrates in peat also affords an additional means of identifying the origin of some peat humic substances. Glucosamine, the monomer from which chitin is formed is found in peat (Fuchsman, 1980). Fungi, especially basidiomycetes, probably are the principal source of peat chitin. Glucosamine may thus be used to estimate part of the fungal contribution to peat organic matter.

(1) Enzymes in peat.

The recognition of microbial activity in peat as the quintessential decomposition process, and the identification of humic substances as products of microbial synthesis poses new questions about peat-water relationships, and suggests new possibilities for the use of peat. The array of techniques of physical chemistry, analytical chemistry, and organic chemistry must now be supplemented by those of biochemistry, especially those of enzymology. Enzymes are the catalysts essential to the processes by which living organisms obtain food, metabolize it, grow, and reproduce. Enzymes of great variety are found in organic soils. Their identification, and the understanding of their modes of existence and action are subjects of detailed investigation in many countries. Nevertheless, familiarity with soil enzymes and the means of studying them is rare among peat scientists.

Although soil enzymes are produced by living organisms, these catalysts exist not only inside living cells, but also as exocellular substances. These exocellular enzymes are relatively immobile large molecules, secreted by nearby cells. They are residues left by the cells of higher plants or of microorganisms which have died and disintegrated, or the products of mobile cells which have moved away from the site where the enzyme was secreted.

The exocellular enzymes differ in role from intracellular enzymes. Away from cells, enzymes function only as specific catalysts, capable of accelerating processes which would otherwise occur spontaneously but more slowly (e.g., hydrolysis of polysaccharides and polypeptides).

These hydrolyses convert insoluble immobile molecules into soluble monosaccharides and amino acids capable of rapid diffusion. The small molecules, reaching the surface of appropriate bacterial or fungal cells are absorbed as food for sustenance and growth.

Enzyme activity, particularly in drained peat, may be commercially disadvantageous. In aerated peat microbial metabolism results in a net consumption of organic matter (e.g., conversion of organic carbon to CO_2). This loss, observable as subsidence in drained peatlands, can be partially counteracted by the addition of small amounts of copper salts. Mathur (1982) concluded that the copper acts by inactivating the enzymes present in peat.

Enzymes, which are themselves protein, are subject to a variety of adverse influences which may inactivate or decompose them. Nevertheless many of these enzymes persist, and can be shown to be biochemically active. Prof. Mayaudon has described in some detail the chemical arrangement of the enzyme components which contribute to their continued activity.

Since the structure of enzymes is genetically determined, it should be possible, by establishing the sequence of amino acids in individual enzymes, to identify the species which generated them. The ecological interrelationships existing in peat would thereby be greatly clarified.

The hydrolysis of polypeptides and of polysaccharides, mediated in nature by soil enzymes, can also be effected by strong acids, and by elevated temperature. However acid-catalyzed hydrolyses are less

specific than those mediated by enzymes and, from an engineering viewpoint, more energy-intensive.

(m) Biotechnology of peat fractions

Hydrolysis converts polysaccharide and polypeptide colloids into soluble organic compounds, so that, in the absence of new growth of microorganisms, the quantity of peat solids decreases, and the organic material dissolved in the aqueous phase increases. Whether such an increase in organic solution constitutes a water pollution problem or a commercial opportunity depends partly on one's viewpoint. To the extent to which the aqueous effluent is biodegradable it is also bio-utilizable. Peat scientists familiar with current developments in the technology of fermentation and of single-cell protein production may view the organic solute as a chemical feedstock. The observations of soil enzymologists provide a basis for developing the needed biotechnology.

Living microorganisms represent an extension of the possibilities inherent in the simple industrial use of enzymes. A larger range of reactions exists for enzymes inside cells, or for enzymes on cell surfaces closely connected with intracellular structures, than for isolated enzymes. While the latter can accelerate only those reactions with a favorable net charge in free energy, cell enzymes can promote the synthesis of even those complex macromolecules whose formation implies an unfavorable net change of free energy. Such otherwise improbable reactions occur only when coupled with appropriate energy-releasing reactions (e.g., oxidative phosphorylation).

It is therefore possible to divide the biochemical reactions in peat into two broad categories. One category can utilize isolated enzymes or other catalysts (e.g., acids or bases), and can thus be considered for industrial use under a wide range of physical conditions. The secondary category requires conditions favoring the growth and multiplication of the appropriate organisms.

The combination of these two enzymatic categories illustrates the significance of mixed microbial populations in nature, where the products of exocellular enzymatic activity induced by one organism can be used for growth and synthesis by other organisms (Fuchsman, 1980).

(n) The effect of heating on dewatering peat.

Wet carbonization embodies several concepts bearing on the dewatering problem. Turbulent mixing of solids in hot aqueous suspension accelerates the physical disintegration of loose aggregates and thereby reduces the likelihood of water occlusion in subsequent pressure filtration. The elevated temperature also increases the solubility of some components, (e.g., hemicelluloses) which, in the solid state, are sites for water retention. The heat also liquifies some low-melting materials (e.g., waxes) which could otherwise obstruct water flow during filtration.

These effects are however small. Significant improvements in the carbon content of the filtered solids require temperatures at which chemical dehydration can occur along with physical dewatering.

Abel (1965) had shown that simple sugars, like glucose, lose weight rapidly at 170°C; starch and hemicelluloses at 250°C; cellulose at 275-290°C; lignin at about 325°C; and humic acids at about 365°C. Although the temperature of maximum decomposition rate depends on the heating rate and sample source, it is evident that carbohydrates, especially non-celluloses, decompose before the more aromatic components. In a Finnish wet carbonization process where peat was heated at 200°C for 30 minutes, the resulting solids could be press-filtered to about 50% moisture, good enough for fuel use (Myreen, 1980). Although Myreen attributed the dewatering success to collapse of the micropore system and compaction of the colloidal particles, about 25% of the initial weight of the peat solids were lost, partly as water and carbon dioxide, partly as dissolved volatile and non-volatile organics. There was evidently extensive chemical breakdown in the peat carbohydrate fraction.

Soviet scientists, in the 1950's in an experimental plant at Boksitogorsk, operated autoclaves in which peat was retained at 185°C (at 12 atmospheres pressure) for 20 minutes, ultimately yielding a filtered briquetted product containing 37-45% water (Fuchsman, 1980). Carbon losses included carbon dioxide, acetic acid, and furfural. Furfural is known to result from the thermal decomposition of pentoses and of hemicelluloses generally.

Weight loss from carbohydrates is primarily water (from dehydration reactions), and carbon dioxide (from decarboxylation of uronic acids). This loss of oxygenated material (H_2O + CO_2) is

accompanied by a relative increase of carbon in the residue, and a corresponding increase in caloric value of the solids. However, such losses of oxygenated compounds must also mean a reduction in the sites for hydrogen-bonding and therefore for water retention by the residual solids.

The thermal degradation of peat components is accompanied by an increase of soluble organic substances in the effluent. The best method for treating this liquid to meet regional water quality standards or for producing marketable by-products requires more detailed chemical and microbiological investigations of the effluent.

Heating peat to dewater it has been studied in a variety of engineering configurations. Chornet et al. (1982) have described a "low severity peat dewatering technology" in which a peat slurry maintained at 190°C for less than 60 seconds is allowed to expand through a nozzle to produce a filtered product with less than 50% moisture. Even under these mild circumstances there are large losses of organic material (presumably from the carbohydrate fraction). The process is, however, simple and does not appear to be costly to operate.

Water-insoluble water-impermeable materials such as the bitumen fraction of peat may alter the course of wet carbonization, although the nature of the effect is difficult to predict. The influence of bituminous matter on the filterability of wet carbonized peat can be tested by comparing the performance of untreated and debituminized samples.

The colloidal and macroporous structures of peat are altered by heating. However, few data are available on the colloidal behaviour or on the hydraulic permeability of heated peat, or on the colloidal properties of the effluent. Detailed carbohydrate analyses of the solid and liquid products are similarly lacking, although such data would be helpful in optimizing thermal treatments. Until these data are developed, progress in wet carbonization will continue to be empirical.

(o) New directions for the study of peat-water relationships.

Chemical interest in water retention mechanisms in peat appears to concentrate on two components: humic acids and carbohydrates. The alteration of these substances may improve the performance of existing dewatering filters.

Carbohydrates are certainly subject to hydrolytic change. Enzymatic or acid-catalyzed hydrolysis may improve subsequent filtration by releasing some of the carbohydrate as soluble sugars. This process is not likely to be economically attractive if the solids are intended only as fuel. If however, revenue from fuel use is supplemented by income from alcohol or protein production using the dissolved by-product sugars, commercial carbohydrate hydrolysis may offer a serious alternative in peat utilization.

Humic acid offers a less convenient substrate for enzymatic attack. Oxidases appear to be more promising catalysts for humic acid degradation. However non-enzymatic approaches may be better. Alteration in pH, in the direction of the isoelectric point, may

precipitate colloidally dispersed material, while the replacement of carboxylic protons by the addition of di- or trivalent cations may at least reduce the pollution control costs of peat dewatering.

(p) Recommendations.

Each participant at the Rivière-du-Loup meeting, and each reader of this book could estabish his own order of research and development priorities on matters related to peat dewatering. Differences in priorities reflect diversity in experience, technical orientation, and sense of urgency. The following recommendations are offered in the hope that they will find an echo of support among those who are close to peat problems on a day-to-day basis.

This list of recommendations is not a priority sequence. Those responsible for allocating funds and personnel for peat investigations will inevitably consider the broader policy objectives which peat research serves, the availability of suitable facilities, and the prospects of technical success, in selecting directions for future research.

There is, however, a need to go beyond conventional planning. The major problems in peat technology transcend disciplinary boundaries, so that substantial progress will involve working in unfamiliar areas and trying novel approaches, with consequent increase in risk of error. The economic rewards should, however, greatly exceed the cost.

While each item on the list which follows should be considered individually, an appropriately integrated effort will require work in many of the areas identified below.

1. Peatlands of potential commercial interest should be mapped stratigraphically to note chemical composition, and to provide estimates of porosity and hydraulic conductivity. The information is of value in the design of both field drainage systems and pressure filtration operations.
2. Methods should be developed for the recovery of dissolved and suspended solids in the effluents from pressure filtration operations. Improved recovery is needed to minimize pollution control costs, and to improve overall product yields.
3. The conversion of peat filter effluents into feedstocks for fermentation and/or protein production operations, using presently available methods of biotechnology should be investigated. The generation of these byproducts should be assessed in terms of overall unit cost for integrated operations (with fuel peat as the principal product).
4. The study of the change in hydraulic permeability of peat during drainage should be extended to include all commercially significant peat types.
5. The study of stress-strain relations in high-pressure filtration of peat should be extended to include systems involving shear stresses, and systems in which the dispersed solids in the effluent are recycled into the feed to the filters.
6. The distribution of hydrophilic and hydrophobic surfaces on peat solids should be investigated in both the natural and partially dried conditions, to obtain insight on the phenomenon of loss of re-wettability on drying.

7. The surface and colloidal properties of peat shouuld be investigated in relation to nitrogen content. Some nitrogen atoms are sites of positive charges among predominantly negatively charged particles. The role of peat nitrogen in colloid chemistry should be more clearly identified.
8. The relationship of geometric form of humic acid aggregates (as seen by electron microscopy) to their origin and method of preparation should be studied to provide an engineering basis for utilizing humic acids.
9. Proximate chemical analyses of peat filter cakes and filter effluents, respectively, should be obtained to provide information on the degree to which humic acids, carbohydrates, and other components move independently during peat dewatering.
10. The water-soluble fraction of peat, generated by the solution and reprecipitation of humic acids, should be analyzed for its content of carbohydrates and other hydrophilic substances.
11. The diffusion rates of humic acids should be investigated as a function of pH and of metal ion concentration, in order to understand anomalous humic acid contents observed in some peat deposits.
12. The use of surfactants, pH control, and metal ion addition, separately and in combination, to aggregate peat colloids to a filterable state should be studied.
13. The effect of metal ions on the hydraulic conductivity and other factors affecting filtration should be investigated.

14. The role of nitrogen in peat should be investigated, particularly with respect to the complexation and retention of metal ions.
15. The water retention properties of native peat should be studied as a multivariate function of chemical composition and of physical parameters. The use of "analysis of variance" and related statistical techniques is recommended.
16. The nature of polysaccharide linkages in peat should be determined as a means of predicting water retention and characterizing the genesis of peat compounds.
17. The nitrogen-containing compounds in peat should be identified to aid in determining the microbial processes in native peat.
18. The identification and level of activity of soil enzymes in peat should be established as a guide to the rapidity of chemical change in peat following drainage and harvesting, and in storage.
19. The chemical compositions of wet-carbonized peat and of the effluent from the wet-carbonization process should be examined more closely to determine the fate of individual peat components (e.g. carbohydrates, humic acids, amino acids, etc.). The variation of these chemical compositions as functions of time and temperature should be developed for the principal types of peat.
20. More information should be developed on the physical properties of peat solids after wet-carbonization, especilly with respect to optimizing filtration conditions.

21. An attempt should be made to correlate the nature and size of microbial populations, and their metabolic activities, to changes in the water-retention characteristics of peat. Such correlations would be of value in determining whether cultivation of suitable microorganisms in the field, or in storage, can improve dewatering properties of peat.

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